→ Radial Equations

$$-\frac{\hbar^2}{2m}\left[\frac{\partial^2}{\partial r^2}+\frac{2}{r}\frac{\partial}{\partial r}+V_{eff}^{(\ell)}(r)\right]R_{n\ell}(r) = E\,R_{n\ell}(r)$$

* Are "n" and "ℓ" enough for $R(r)$?

i) ℓ : obvious ← $V_{eff}^{(\ell)}$

ii) n : "Sturm - Liouville" theory : bound states are non-deg. and Real, in 1D. (See also HW#5.1)

Thus, $\langle\vec{x}\,|\,n,\ell,m\rangle \equiv R_{n\ell}(r)\,Y_\ell^m(\theta,\phi)$

↑ radial eq. ↑ eigenfunction of $\vec{L}^2$ and L_z.

④ Spherical Harmonics : $Y_\ell^m(\theta,\phi) = \langle\hat{n}\,|\,\ell,m\rangle$ $\quad \hat{n}=\frac{\vec{x}}{|\vec{x}|}$

$$L_z\,|\ell,m\rangle = m\hbar\,|\ell,m\rangle \quad \cdots\cdots (*)$$

$$\vec{L}^2\,|\ell,m\rangle = \ell(\ell+1)\hbar^2\,|\ell,m\rangle \quad \cdots\cdots (**)$$

i)

$\langle\hat{n}|\cdot(*)$: $-i\hbar\frac{\partial}{\partial\phi}Y_\ell^m(\theta,\phi) = m\hbar\,Y_\ell^m(\theta,\phi)$

→ $Y_\ell^m(\theta,\phi) \propto \exp[\,im\phi\,]$

∴ Integer m's are only allowed !

Here, we're talking about "spatial" wave-functions.

→ $\psi(r,\theta,0) = \psi(r,\theta,2\pi)$ to be single-valued in "position space"

☆☆☆ m = integers : $-\ell,-\ell+1,\cdots\ell-1,\ell$.

So, ↳ ℓ = integers. ☆☆☆ for the "orbital" angular momentum.

ii) $\langle \hat{n} | \cdot (**)$:

$$\left[\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial}{\partial\theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} + l(l+1) \right] Y_l^m(\theta,\phi) = 0$$

- Approach 1 : You can just solve the diff. eq.

↳ $\left[\left(\sin\theta \frac{\partial}{\partial\theta} \right)^2 + \frac{\partial^2}{\partial\phi^2} \right] Y_l^m(\theta,\phi) = -l(l+1)\sin^2\theta \, Y_l^m(\theta,\phi)$

: θ and ϕ are seperable, $Y_l^m(\theta,\phi) = e^{im\phi} \cdot f_l^m(\theta)$

and by setting $x \equiv \cos\theta$, $f_l^m(\theta) \to P_l^m(\cos\theta)$

↳ $\frac{d}{dx}\left[(1-x^2) \frac{dP_l^m}{dx} \right] + \left[l(l+1) - \frac{m^2}{1-x^2} \right] P_l^m(x) = 0$.

↳ $P_l^m(x)$: the associated Legendre function.

$$\Rightarrow Y_l^m(\theta,\phi) = \sqrt{\frac{2l+1}{4\pi} \frac{(l-m)!}{(l+m)!}} (-1)^m e^{im\phi} P_l^m(\cos\theta). \quad \text{for } m \geq 0$$

for $m < 0$, use $Y_l^{-m}(\theta,\phi) = (-1)^m \left[Y_l^m(\theta,\phi) \right]^*$

↑ a property of P_l^m.

Normalization :

$\int d\Omega \, Y_{l'}^{m'*} Y_l^m = \delta_{ll'} \delta_{mm'}$ // $\int d\Omega = \int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta \, d\theta$

↑ Solid angle

Associated Legendre function :

$$P_l^m(x) = (-1)^m (1-x^2)^{\frac{m}{2}} \frac{d^m}{dx^m} P_l(x) \quad // \ m \geq 0$$

↑ Legendre polynomial.

- Approach 2 : compute $\langle \hat{n} | l, l \rangle$; lower with L_-.

$L_+ |l, l\rangle = 0$: $-i\hbar e^{i\phi} \left[i \frac{\partial}{\partial\theta} - i \cot\theta \frac{\partial}{\partial\phi} \right] Y_l^l(\theta,\phi) = 0$

$$\Rightarrow \quad Y_l^l(\theta,\phi) = C_l \, e^{il\phi} \sin^l\theta$$

use the normalization to determine C_l.

$$\Rightarrow \quad |C_l|^2 \int_0^{2\pi} d\phi \int_{-1}^{1} d(\cos\theta) \, \sin^{2l}\theta = 1$$

$$\hookrightarrow \int_{-1}^{1} dx \, (1-x^2)^l = \cancel{\frac{x}{1}(1-x^2)^l \Big|_{-1}^{1}} \to 0 - \int_{-1}^{1} dx \; x \cdot l \cdot (1-x^2)^{l-1} \cdot (-2x)$$

(int. by parts)

$$= l \cdot \cancel{\frac{2}{1\cdot 3} x^3 (1-x^2)^{l-1} \Big|_{-1}^{1}} \to 0 - \int_{-1}^{1} dx \; \frac{2}{3} x^3 \cdot l(l-1)(1-x^2)^{l-2} \cdot (-2x)$$

$$= l \cdot (l-1) \cancel{\frac{2 \cdot 2}{1 \cdot 3 \cdot 5} x^5 (1-x^2)^{l-2} \Big|_{-1}^{1}} \to 0 - \int_{-1}^{1} \cdots$$

$\vdots$

$$= l! \cdot \frac{2^l}{(2l+1)!!} \cdot 2 = \frac{(2^l \, l!)^2}{(2l+1)!} \cdot 2$$

$$\Rightarrow \quad |C_l|^2 \cdot \frac{(2^l \, l!)^2}{(2l+1)!} \cdot 4\pi = 1$$

$$C_l = e^{i\alpha} \cdot \frac{1}{2^l \, l!} \sqrt{\frac{(2l+1)!}{4\pi}}$$

choose $e^{i\alpha} = (-1)^l$: To obtain Y_l^0 with the same sign as $P_l(\cos\theta)$.

$$\Rightarrow \quad C_l = \frac{(-1)^l}{2^l \, l!} \sqrt{\frac{(2l+1)!}{4\pi}}$$

↑ It's convention.

$$\Rightarrow Y_\ell^\ell(\theta,\phi) = \frac{(-1)^\ell}{2^\ell \ell!}\sqrt{\frac{(2\ell+1)!}{4\pi}}\, e^{i\ell\phi}\sin^\ell\theta$$

To lower m, use $L_-|\ell,m\rangle = \sqrt{(\ell+m)(\ell-m+1)}\,\hbar\,|\ell,m-1\rangle$

Step 1.

$$\left(\frac{L_-}{\hbar}\right)|\ell,\ell\rangle = \sqrt{2\ell\cdot 1}\,|\ell,\ell-1\rangle$$

$$\left(\frac{L_-}{\hbar}\right)^2|\ell,\ell\rangle = \sqrt{2\ell\cdot 1}\left(\frac{L_-}{\hbar}\right)|\ell,\ell-1\rangle = \sqrt{2\ell\cdot(2\ell-1)\cdot 1\cdot 2}\,|\ell,\ell-2\rangle$$

$$\vdots$$

$$\left(\frac{L_-}{\hbar}\right)^{\ell-m}|\ell,\ell\rangle = \sqrt{2\ell\cdot(2\ell-1)\cdots(\ell+m+1)\cdot 1\cdot 2\cdots(\ell-m)}\,|\ell,m\rangle$$

$$= \sqrt{\frac{2\ell!\,(\ell-m)!}{(\ell+m)!}}\,|\ell,m\rangle$$

$$\Rightarrow Y_\ell^m(\theta,\phi) = \sqrt{\frac{(\ell+m)!}{2\ell!\,(\ell-m)!}}\left(\frac{L_-}{\hbar}\right)^{\ell-m}|\ell,\ell\rangle$$

Step 2

$$\left(\frac{L_-}{\hbar}\right)Y_\ell^\ell = +e^{-i\phi}\left(-\frac{\partial}{\partial\theta} + i\cot\theta\frac{\partial}{\partial\phi}\right)Y_\ell^\ell$$

$$= -C_\ell\, e^{i(\ell-1)\phi}\left(\frac{\partial}{\partial\theta} + \ell\cot\theta\right)\sin^\ell\theta$$

$$= -C_\ell\, e^{i(\ell-1)\phi}\cdot\frac{1}{\sin^\ell\theta}\frac{\partial}{\partial\theta}\left(\sin^\ell\theta\cdot\sin^\ell\theta\right) \qquad \left\| \ \frac{\partial}{\partial\cos\theta} = -\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\right.$$

$$= C_\ell\, e^{i(\ell-1)\phi}\cdot\frac{1}{\sin^{\ell-1}\theta}\frac{\partial}{\partial\cos\theta}\sin^{2\ell}\theta$$

$$\left(\frac{L_-}{\hbar}\right)^2 Y_\ell^\ell = -C_\ell\, e^{i(\ell-2)\phi}\left(\frac{\partial}{\partial\theta} + (\ell-1)\cot\theta\right)\left(\underline{\frac{1}{\sin^{\ell-1}\theta}\frac{\partial}{\partial\cos\theta}\sin^{2\ell}\theta}\right)$$

$$= -C_\ell\, e^{i(\ell-2)\phi}\,\frac{1}{\sin^{\ell-1}\theta}\frac{\partial}{\partial\theta}\left(\sin^{\ell-1}\theta\cdot\left(\ \downarrow\ \right)\right)$$

$$= C_\ell\, e^{i(\ell-2)\phi}\,\frac{1}{\sin^{\ell-2}\theta}\left(\frac{\partial}{\partial\cos\theta}\right)^2\sin^{2\ell}\theta$$

$$\vdots$$

$$\Rightarrow \left(\frac{L_-}{\hbar}\right)^{\ell-m}Y_\ell^\ell(\theta,\phi) = C_\ell\, e^{im\phi}\,\frac{1}{\sin^m\theta}\left(\frac{\partial}{\partial\cos\theta}\right)^{\ell-m}\sin^{2\ell}\theta$$

holds for $m\geq 0$. (at $m=0$, $\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\cdots$)

$$\Rightarrow \quad Y_\ell^m(\theta,\phi) = \frac{(-1)^\ell}{2^\ell \ell!}\sqrt{\frac{(2\ell+1)}{4\pi}\cdot\frac{(\ell+m)!}{(\ell-m)!}}\, e^{im\phi}\frac{1}{\sin^m\theta}\left(\frac{d}{d\cos\theta}\right)^{\ell-m}\sin^{2\ell}\theta$$

for $m \geq 0$.

Using Rodrigues' formula : $P_\ell(x) = \frac{1}{2^\ell \ell!}\frac{d^\ell}{dx^\ell}(x^2-1)^\ell$

$$= \frac{(-1)^\ell}{2^\ell \ell!}\frac{d^\ell}{dx^\ell}(1-x^2)^\ell$$

$$Y_\ell^0(\theta,\phi) = \sqrt{\frac{2\ell+1}{4\pi}}\, P_\ell(\cos\theta)$$

That's why we need $(-1)^\ell$ in C_ℓ.

- One can also start from $m=-\ell$:

$$Y_\ell^{-\ell}(\theta,\phi) = \frac{1}{2^\ell \ell!}\sqrt{\frac{(2\ell+1)!}{4\pi}}\, e^{-i\ell\phi}\sin^\ell\theta$$

No extra phase $(-1)^\ell$ is given !

Applying $\left(\frac{L_+}{\hbar}\right)^{\ell+m}$, $m \leq 0$

$$Y_\ell^m(\theta,\phi) = \frac{(-1)^{\ell+m}}{2^\ell \ell!}\sqrt{\frac{(2\ell+1)}{4\pi}\cdot\frac{(\ell-m)!}{(\ell+m)!}}\, e^{im\phi}\sin^m\theta\left(\frac{d}{d\cos\theta}\right)^{\ell+m}\sin^{2\ell}\theta$$

prove it by yourself !

$$\Rightarrow \quad Y_\ell^0(\theta,\phi) = \sqrt{\frac{2\ell+1}{4\pi}}\, P_\ell(\cos\theta).$$

and it verifies $Y_\ell^{-m}(\theta,\phi) = (-1)^m\left[Y_\ell^m(\theta,\phi)\right]^*$.

Summary.

Thus. $$Y_\ell^{|m|}(\theta,\phi) = \frac{(-1)^\ell}{2^\ell \ell!}\sqrt{\frac{(2\ell+1)}{4\pi}\frac{(\ell+|m|)!}{(\ell-|m|)!}}\, e^{i|m|\phi}\frac{1}{\sin^{|m|}\theta}\left(\frac{d}{d\cos\theta}\right)^{\ell-|m|}\sin^{2\ell}\theta.$$

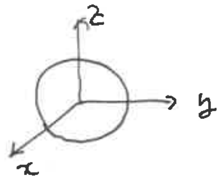
and,

$$Y_\ell^{-|m|}(\theta,\phi) = (-1)^{|m|}\left[Y_\ell^{|m|}(\theta,\phi)\right]^*.$$

... Spherical Harmonics.

* Plots of $|Y_\ell^m(\theta,\phi)|^2$

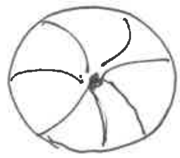
$Y_0^0(\theta,\phi) = \sqrt{\frac{1}{4\pi}}$ ……



$\longrightarrow$ s-orbital.

$Y_1^{\pm 1}(\theta,\phi) = \mp\sqrt{\frac{3}{8\pi}}\, e^{\pm i\phi}\sin\theta$

$= \mp\sqrt{\frac{3}{8\pi}}\, \frac{x \pm iy}{r}$ …



donut.

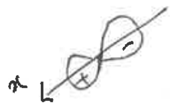
$Y_1^0(\theta,\phi) = \sqrt{\frac{3}{4\pi}}\cos\theta$ …

$= \sqrt{\frac{3}{4\pi}}\,\frac{z}{r}$ …

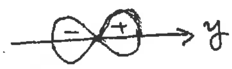
$\longrightarrow$ p-orbitals

p-orbitals "

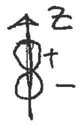
* p_x-orbital $\Leftarrow \frac{1}{\sqrt{2}}\left(Y_1^{-1} - Y_1^{1}\right) \propto \frac{x}{r}$



$p_y \Leftarrow \frac{i}{\sqrt{2}}\left(Y_1^{-1} + Y_1^{1}\right) \propto \frac{y}{r}$



$p_z \Leftarrow Y_1^0 \propto \frac{z}{r}$



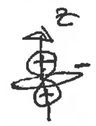
One node in $(0,\pi)$.

$Y_2^{\pm 2} = \sqrt{\frac{15}{32\pi}}\, e^{\pm 2i\phi}\sin^2\theta = \sqrt{\frac{15}{32\pi}}\,\frac{x^2 - y^2 \pm i xy}{r^2}$

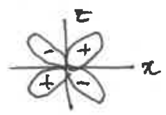
$Y_2^{\pm 1} = \mp\sqrt{\frac{15}{8\pi}}\, e^{\pm i\phi}\sin\theta\cos\theta = \mp\sqrt{\frac{15}{8\pi}}\,\frac{z(x \pm iy)}{r^2}$

$Y_2^0 = \sqrt{\frac{15}{16\pi}}\left(3\cos^2\theta - 1\right) = \sqrt{\frac{15}{16\pi}}\,\frac{3z^2 - r^2}{r^2}$

$d_{z^2} \Leftarrow Y_2^0 \propto \frac{3z^2 - r^2}{r^2}$ ……



$d_{xz} \Leftarrow \frac{1}{\sqrt{2}}\left(Y_2^{-1} - Y_2^{1}\right) \propto \frac{xz}{r^2}$ ……

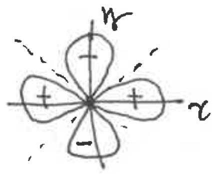


$d_{yz} \Leftarrow \frac{i}{\sqrt{2}}\left(Y_2^{-1} + Y_2^{1}\right) \propto \frac{yz}{r^2}$ …… similar

Two nodes

$d_{xy} \Leftarrow \frac{i}{\sqrt{2}}\left(Y_2^{-2} - Y_2^{2}\right) \propto \frac{xy}{r^2}$

$d_{x^2-y^2} \Leftarrow \frac{1}{\sqrt{2}}\left(Y_2^{-2} + Y_2^{2}\right) \propto \frac{x^2 - y^2}{r^2}$ ……



"d" - orbitals